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| 13. ABSTRACT (Maximum 200 words) This AASERT project has explored the capability of a new tracking-based algorithm for extracting high quality potential surfaces from time-dependent laboratory data. The algorithm is based on a special inversion technique for tracking the temporal data as a means to extract its underlying potential surface information. The basic concepts for the algorithm have now been developed and successfully tested in several simulations. An attractive feature of the algorithm is its parallel structure with quantum mechanical control techniques, thus ultimately opening up the prospect of combining control and inversion of molecular dynamics into a single cooperative laboratory-based venture. | | | | |
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Princeton University
Department of Chemistry

**“EXTRACTION OF HIGH QUALITY POTENTIAL
SURFACES FROM LABORATORY DATA”**

Contract Number F49620-93-I-0300

FINAL TECHNICAL REPORT

to the Air Force Office of Scientific Research
for the Period of May 15, 1993 - May 31, 1996

Prepared by
Herschel Rabitz, Principal Investigator

1 Introduction

The extraction of molecular Hamiltonian information from laboratory data has been a goal of considerable importance in chemistry. In general, the data can come from either stationary or time-dependent experiments, with the latter just recently becoming available at interesting ultrashort time scales[1]. In addition, there are numerous spectroscopic, and other sources, of time-independent data. A significant bottleneck in this field has been the lack of reliable algorithms for inverting such data to their underlying physical (Hamiltonian) information[2, 3, 4, 5, 6].

The algorithm presented in this work may be traced back to tracking control of molecular motion[7]. In the inversion context, a "track" $\langle O(t) \rangle$ was assumed to be observed laboratory data, and the goal was to find the potential or electric dipole function consistent with the track. This report presents the basic rudiments of the idea that was developed under this project, and the results suggested that the concepts were quite well-founded.

A variety of dynamical experiments[8] and theoretical techniques provided the basis for the inversion research. The last three decades witnessed the development of time-dependent quantum-mechanical methods for molecular dynamics[9], which were made possible by the efficient numerical algorithms of wavepacket propagation[10]. Combining the advances in both the experimental and the numerical techniques, we proposed a new inversion algorithm that reconstructs the underlying potential energy surfaces (PES) and dipole function from temporal measurements.

2 Methodology

Different types of observables and different initial conditions can arise, depending on the nature of the experiments. Here, we consider a single observable operator \hat{O} with a sequence of initial conditions $\psi_j(t=0), j=1, 2, \dots, N_D$. The Hermitian operator \hat{O} corresponded to a physical quantity observed in laboratory as a function of time. For example, in the case of position tracking, $\hat{O} = x$, and $\langle x(t) \rangle$ is the measured mean position of the atoms in the molecule (e.g., measurement of ultrafast X-ray or electron diffraction).

The experiments were assumed to provide measurements $\langle O_j(t) \rangle = \langle \psi_j(t) | \hat{O} | \psi_j(t) \rangle$, $j=1, 2, \dots, N_D$. According to the Heisenberg equation of motion, we had

$$\begin{aligned} i\hbar \frac{d\langle O_j \rangle}{dt} &= \langle \psi_j | [\hat{O}, H] | \psi_j \rangle \\ &= \langle \psi_j | [\hat{O}, T] | \psi_j \rangle + \langle \psi_j | [\hat{O}, V] | \psi_j \rangle - \epsilon_j(t) \langle \psi_j | [\hat{O}, \mu] | \psi_j \rangle \end{aligned} \quad (1)$$

where $H = T + V - \mu\epsilon(t)$ was the Hamiltonian for the system, T was the kinetic energy operator, $\mu(x)$ was the dipole moment and $\epsilon(t)$ was an external field.

For any arbitrary Hermitian operator \hat{O} , Eq. (1) could be recast into the form of a Fredholm integral equation of the first kind for the potential

$$\int K(j, x) V(x) dx = g_j \quad (2)$$

where

$$\begin{aligned} g_j &= \frac{\hbar}{2} \frac{d\langle O_j \rangle}{dt} - \text{Im} \langle \psi_j | \hat{O} (T - \epsilon\mu) | \psi_j \rangle, \\ K(j, x) &= \text{Im} \{ (\hat{O}\psi_j)^* \psi_j \} \end{aligned} \quad (3)$$

A similar expression could be written for the dipole function, if it was also sought. The kernels $K(j, x)$ in Eq. (3) implicitly depended on time. We assumed that $[\hat{O}, V]$

was not identically zero. If $[\hat{O}, V] \equiv 0$, then Eq. (1) was not an invertible relation as it stood. In such a case, the differentiation of the track $\langle O_j(t) \rangle$ with respect to time must be continued to obtain a higher-order equation which is invertible[11]. An example was the case of position tracking $\hat{O} = x$. Although $[x, V(x)] = 0$, the invertible relation for V was obtained after differentiating $\langle x(t) \rangle$ twice with respect to time.

Given the above basic relations, a family of algorithms was suggested to achieve the desired inversion. Many issues arose in this regard, and only the simplest approach was explored in the research. The procedure for the potential inversion is given below in detail, based on the field $\varepsilon(t)$ being zero. This discussion can be easily adapted to the dipole inversion case. The actual laboratory data $\langle O_j(t) \rangle$ is a convolution of the wavefunction in configuration space (or some other representation), and thus, no unique wavefunction ψ_j corresponded to the data. To start the inversion, a set of initial conditions $\psi_j(t=0)$ was needed to be consistent with $\langle \psi_j(0) | \hat{O} | \psi_j(0) \rangle = \langle O_j(t=0) \rangle$, and much freedom existed in the choice. With the known initial states $\psi_j(t=0)$ and the initial data $\langle O_j(t=0) \rangle$, the unknown potential V was the solution of the integral equation (2). Since the initial nonstationary states $\psi_j(0)$ are usually localized in the Franck-Condon region in an electronic excitation process, the solution of the integral equation consequently only gave the local potential V_0 in the Franck-Condon region. However, this piece of potential V_0 could be used to propagate the wavefunctions $\psi_j(0)$ to the next time $\psi_j(\Delta t)$ according to the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial |\psi_j\rangle}{\partial t} = (T + V) |\psi_j\rangle \quad (4)$$

Then, the solution of the integral equation (2) gave the next piece of the potential $V_{\Delta t}$. With $V_{\Delta t}$, the wavefunctions at the next time step $\psi_j(2\Delta t)$ could be obtained by

propagation, which allows for solving the integral equation to get $V_{2\Delta t}$, etc. This procedure could be effected in terms of the split operator method[12]. The process of inversion plus propagation continued until the wavefunctions sampled all dynamically accessible regions of the PES. Finally, the potential V was the union of the sampled pieces along the track.

3 The Need for Regularization

The solution of the integral equation (2) was generally not unique. This was due to the limited information we could get from the inevitably incomplete data. In addition, the solution was likely not stable against small changes in the data, which were known as *ill-posedness*. Both of these issues are common to virtually all inverse problems. However, we did not seek an arbitrary potential or dipole function, but a physical one which was capable of reproducing the data and also met some fundamental physical requirements and boundary conditions. These requirements and conditions constituted our *prior knowledge* about the potential or dipole function. For example, the physical PES should be a *smooth* function and *negligible* asymptotically as $x \rightarrow \infty$. As a general inverse-problem approach was adopted in this research, we did not assume any biased functional form for the potential. Without further restriction, this allowed multiple solutions satisfying Eq. (2), with some of them highly irregular and even singular. The incorporation of prior knowledge provided some mild general constraints on the solutions. Thus, by incorporating this prior knowledge, the solution could be stabilized, which is referred as a *regularization procedure*. Here, we used the very mild criterion of smoothness of the potential as our prior knowledge to regularize the solution.

In order to implement the regularization, Eq. (2) was rewritten as [2]

$$\int K^{[n]}(j, x) V^{[n]}(x) dx = g_j \quad (5)$$

where

$$\begin{aligned} V^{[n]}(x) &= \frac{d^n V}{dx^n}, \\ K^{[n]}(j, x) &= - \int_{x_{min}}^x K^{[n-1]}(j, x') dx' \end{aligned} \quad (6)$$

The regularized solution of Eq. (2) was achieved by minimizing the following functional[2]

$$J = \left\| \int K^{[n]}(j, x) V^{[n]}(x) dx - g_j \right\|_2^2 + \alpha \|V^{[n]}(x)\|_2^2 \quad (7)$$

leading to

$$V_\alpha^{[n]}(x) = \sum_{j=1}^{N_D} \frac{(u_j^T g)}{\omega_j^2 + \alpha} \omega_j v_j(x) \quad (8)$$

where $u_j, v_j(x)$ were the singular functions for the kernel in Eq. (5), with singular values ω_j .

The regularization parameter α denoted the *trade-off* between reproducing the data and the solution being smooth. We constructed an error function of α ,

$$Error(\alpha) = \left\| \int K^{[n]}(j, x) V_\alpha^{[n]}(x) dx - g_j \right\|_2^2 \quad (9)$$

The optimal α^* was located at the global minimum of this error function.

The inversion was actually achieved through the n^{th} derivative $V^{[n]}(x)$, which imposed a stronger smoothness condition on $V(x)$ for $n \geq 1$. To obtain $V(x)$, we needed to integrate n times

$$V^{[m-1]}(x) = - \int_x^\infty dx' V^{[m]}(x') \quad (10)$$

The above proposed algorithm was presented in one dimension, but it could be generalized to higher dimensions as well.

4 Example

We simulated the inversion of the potential and dipole function of a diatomic molecule. Suppose that the mean positions $\langle x_j(t) \rangle = \langle \psi(t)|x|\psi(t) \rangle$ of the wavepackets could be measured in the experiment (e.g., by ultrafast X-ray or electron diffraction). Since the Hessian Eq. (1) for $\hat{O} = x$ was not invertible, the second derivative could be invoked to give

$$\frac{d^2}{dt^2} \langle x_j(t) \rangle = - \int dx |\psi_j|^2 V^{[1]}(x) + \int dx \epsilon(t) |\psi_j|^2 \mu^{[1]}(x) \quad (11)$$

where the superscript 1 denoted the first order space derivative.

We proceeded to reconstruct the potential and the permanent dipole functions from the time-dependent data $\langle x_j(t) \rangle$ by solving the Fredholm integral equation of the first kind, Eq. (2). We applied the direct inversion procedure to a model problem of a bound diatomic molecule.

In the simulation, the initial wavefunctions were taken as Gaussian wavepackets,

$$\psi_{q_{0j}, p_{0j}}(x) = C \exp \left(\frac{i}{\hbar} p_{0j} x - \frac{(x - q_{0j})^2}{2\hbar} \right), \quad j = 1, 2, \dots, N_D \quad (12)$$

where $C = (\pi\hbar)^{-1/4}$ was the normalization constant. The initial condition in Eq. (12) was consistent with the track $\langle x_j(t) \rangle$.

The results presented below were based on the following conditions. The second derivative of the potential was required to be smooth, *i.e.*, $n = 2$. The number of data is $N_D = 16$, $p_{0j} = 0$, $q_{0j} = -0.9 + (j - 1)\Delta x$ where $\Delta x = 0.01$ was the numerical grid spacing; and $x_{min} = -2$, $x_{max} = 8$ specified the size of the numerical grid.

The inverted potential was compared with the exact one V in Fig. 1a. The overall quality of the inverted potential was excellent. As a more sensitive verification, the wavefunction at fixed interval of time was compared to those obtained by the

propagation on the exact potential $V(x)$ (so-called exact wavefunctions) in Fig. 1b. The wavefunctions propagated on the inverted potential had no essential difference from the exact ones, except that a small fluctuation was visible at later times, which resulted from the finite size of the chosen numerical grid. A similar inversion was carried out to extract the dipole function in this model, and the results for the dipole function are given in Fig. 2. Similar quality excellent results were obtained for the inversion.

5 Conclusion

This report summarizes a new direct inversion algorithm under development for recovering molecular potentials and dipole functions from sequential time measurements. The direct algorithm exploits efficient numerical methods of wavepacket propagation. Time is explicitly utilized as an important parameter in organizing the inversion. We have demonstrated this algorithm in a simulation for recovering the potential and dipole moment for a model diatomic molecule.

The proposed inversion algorithm is direct and computationally efficient. The traditional time-independent inversion schemes usually require many iterations before convergence. This can be very time consuming computationally. In the tracking method, the inverse problem is solved just once at each time step. Furthermore, the size of the inverse problem solved in the direct approach can be much smaller ($N_D \approx 10$) than that in the time-independent methods ($N_D \approx 10^2$ in one dimension), because the potential sampled by the localized wavepackets can be inverted locally which is in contrast to the global potential sampled by all the eigenstates or the continuum states. In the direct method most of the computational effort deals with

the wavepacket propagation, which is much easier.

The time-dependent tracking approach to inversion also opens up the possibility to recover the potential from time-independent data, since the latter data can be synthesized from the time-independent information. This topic, as well as a host of other issues, needs to be explored to fully exploit the capabilities of the direct algorithm. The results of this research opens up this field for further exploration of these new concepts of laboratory data inversion.

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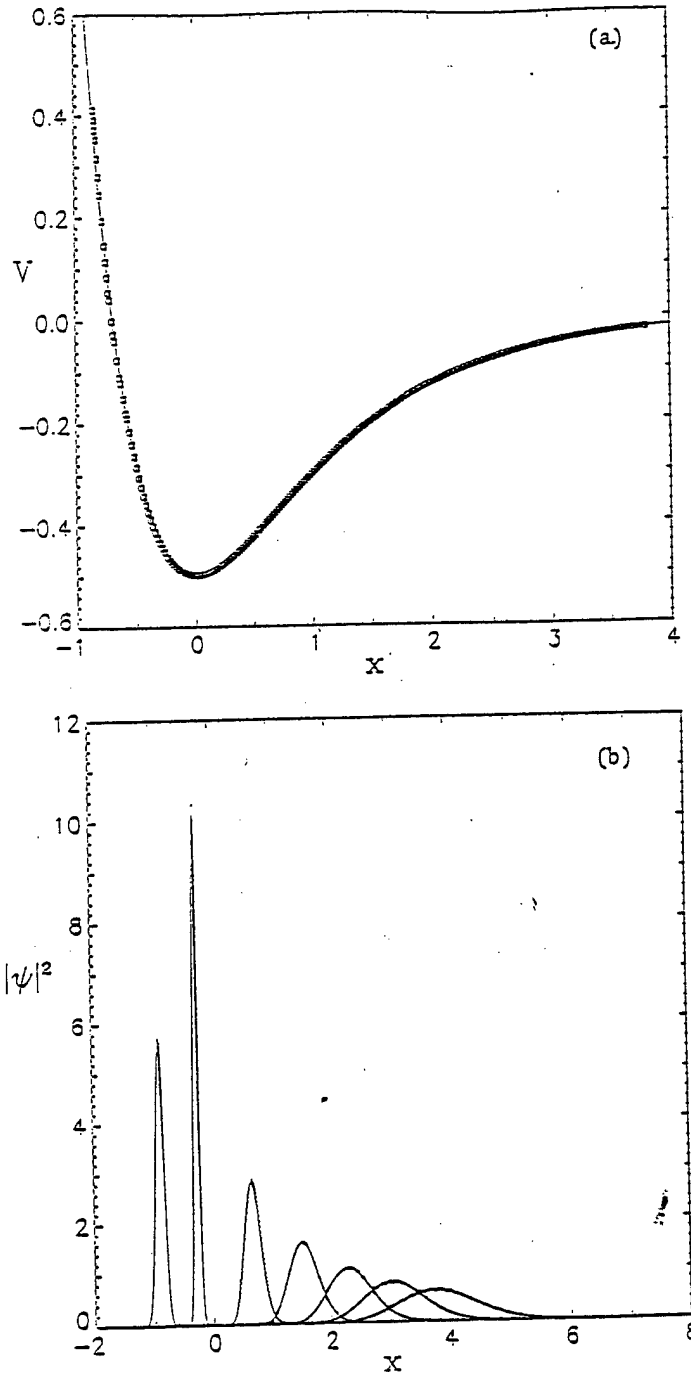


Fig. 1 : The results for the potential inversion. The initial conditions are: $q_{01} = -0.9$ and $p_0 = 0$.

(a) $V(x)$. The squares are the inverted results, and the solid line is the exact potential.

(b) Snapshots of $|\psi_{j=1}|^2$ at the successive intervals of time, where the solid line is recorded during the inversion and dotted line is the exact result obtained by the propagation on $V_M(x)$.

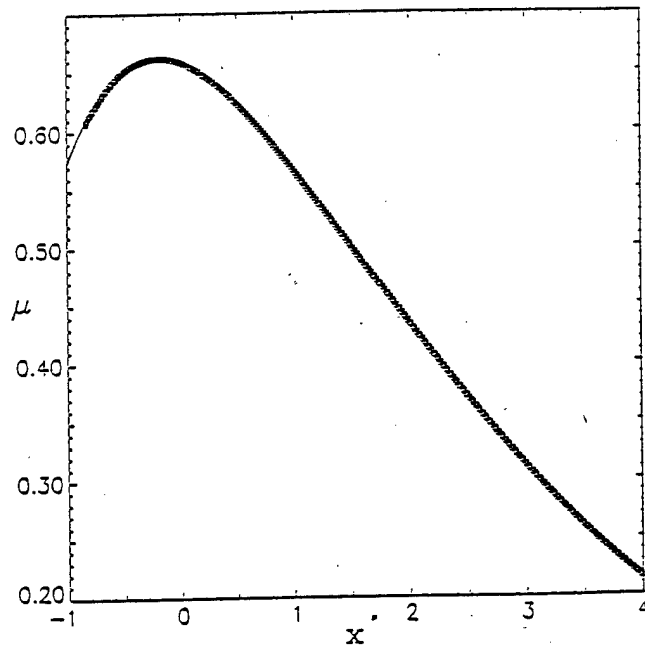


Fig. 2 : The results for the dipole function inversion. The initial conditions are: $q_{01} = -0.9$ and $p_0 = 0$, and $\mu(x)$. The squares are the inverted results, and the solid line is the exact dipole.